

PATENT SPECIFICATION

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(54) POLYMERS CONTAINING QUATERNARY AMMONIUM GROUPS

(71) We, CALGON CORPORATION, a corporation duly organised and existing under the laws of the State of Delaware, United States of America, of Route 60—Campbell's Run Road, Robinson Township, Pennsylvania, United States of America, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

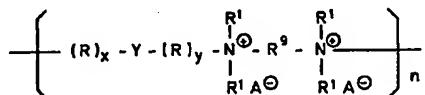
described in and by the following statement:—
This invention is concerned with functional ionene polymers and their use. The term "aliphatic ionene" was first suggested by A Rembaum and his co-workers [Polymer Letters, 6, 160, (1968)] as a generic name for ionic amines, and the term has since gained acceptance in the field of polyelectrolyte chemistry. The term "ionene" is thus used herein to denote polymers containing ionic amine groups, particularly quaternary ammonium groups.

15 quaternary ammonium groups.

The term "functional" is used herein to denote substituent groups appended to the nitrogen atoms of the quaternary ammonium polymer backbone and derived from chemical groups, that is, molecules characterised by recognised chemical activity, in a manner that will be later described herein.

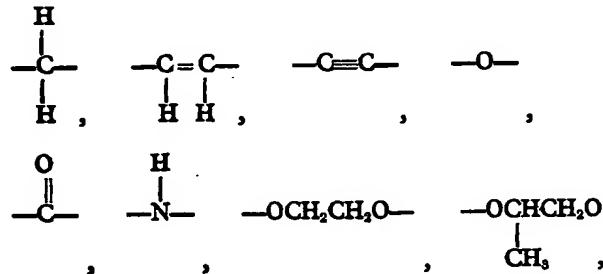
Useful applications of polymeric quaternary ammonium salts have been known for a long time, but up to the present time, investigation and development in the area of ionenes has concerned itself with the building of ionene structures with the end view of providing novel cationic polymers, and utilising that cationic structure for some application that depends on the cationic function of the polymer. Little attention has been paid to the make up of the groups attached to the nitrogen atoms forming the backbone of the cationic polymer structure, and these groups have consequently been confined generally to simple alkyl groups.

25 The novel functional ionene polymers of this invention are represented by the formula:



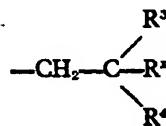
in which R^9 is an alkylene group;

30 in which R' is an alkylene group,
R represents the group CH_2 and/or a substituted CH_2 group in which one of the hydrogen atoms of the group is replaced by alkyl or hydroxymethyl;
Y is



$-\text{OCH}_2\text{O}-$, $-\text{S}-$, $-\text{SO}-$, $-\text{SO}_2-$ or arylene;

in which R^1 is a C_{1-4} alkyl or C_{2-4} alkenyl radical or a radical of formula

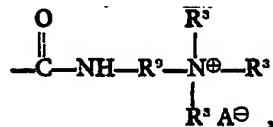
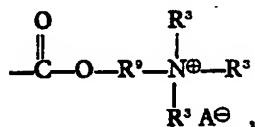
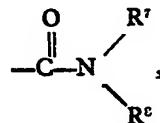
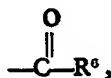
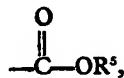
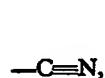


R^x is hydrogen or C_{1-4} alkyl,

5 R^3 is hydrogen, halogen, alkyl, cycloalkyl, aryl, alkaryl, or aralkyl, and

R^4 is

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10 where R^3 and R^9 are as defined above;

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R^5 is alkyl, cycloalkyl, or alkoxyalkyl;

R^6 is alkyl, cycloalkyl, alkoxyalkyl or aryl;

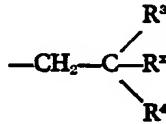
each of R^7 and R^8 is, independently of the other, hydrogen, alkyl, cycloalkyl, aryl, alkaryl, aralkyl, or alkoxyalkyl;

15 A^{\ominus} is an anion;

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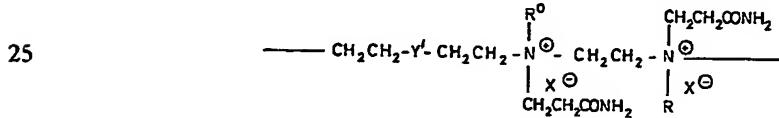
x and y are integers from 1 to 10; and

n is an integer; provided that at least one R^1 is a group of formula:



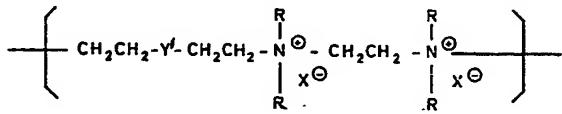
20 The polymers of the present invention are derived from cationic polyelectrolyte structures based on ionic amine backbones. The polymers of this invention, however have attached to the nitrogen atoms of the polymer backbone a number of different functional groups, the characteristics of which groups result in compositions useful in a variety of ways. Among preferred polymers in accordance with the present invention are those having recurring units of formula:

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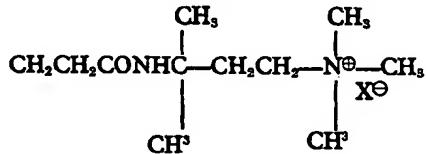


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and those having recurring units of formula:



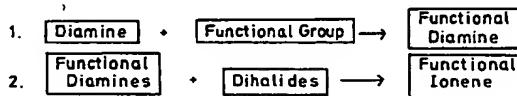
in which R^0 is CH_3 or $CH_2CH_2CONH_2$;
 R is



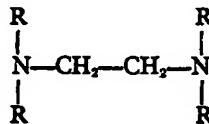
X is Cl or Br; and Y' is oxygen or nothing.

The functional ionene polymers of this invention may be prepared, and have been found to be useful, with a wide range of molecular weights. The average molecular weight may be as low as 300 or as high as or higher than 300,000. Thus, n may be an integer of 2 to 1000 or more. The average molecular weight of the polymer will be determined by the requirements of the particular use to which it is put.

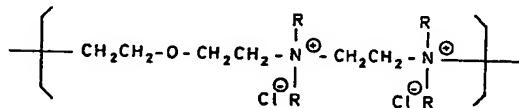
The novel functional ionene polymers of this invention are prepared in what is essentially a two-step process using three basic chemical structure materials. This two-step process may be conveniently illustrated by the following flow diagram:



A simple example will serve to better illustrate this preparation method. In this example the basic diamine building block is ethylene diamine. This diamine is reacted with acrylamide by way of the Michael addition to give the following functional diamine:

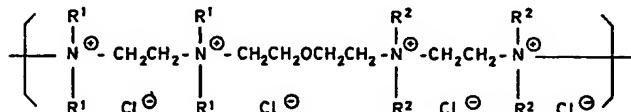


where R is $\text{CH}_2-\text{CH}_2-\text{CONH}_2$. In this example the ethylene diamine has been completely reacted so as to produce a diamine fully substituted with propionamido groups. However, such complete substitution is not necessary, and this invention also contemplates lesser degrees of substitution, but does require the substitution of at least one functional group. The diamine fully substituted with propionamido groups is next reacted with a dihalide, which in this example is bis-chloroethylene. A functional ionene with the following repeating unit results:



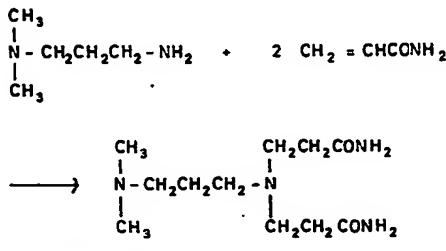
where R is $\text{CH}_2-\text{CH}_2-\text{CONH}_2$.

By utilizing more than one type of substituted functional diamine, a greatly increased number of different functional ionene structures is possible. For example, in addition to the tetrapropionamidoethylenediamine employed above, it is possible to use additionally tetraallylethylenediamine in the reaction with bis-chloroethylether. The following functional ionene repeating unit results:

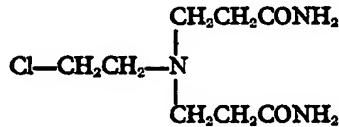


where R^1 is $CH_2CH_2CONH_2$ and R^2 is $CH_2CH=CH_2$.

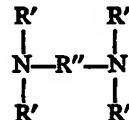
It is also possible to prepare mixed functional diamines, and this invention contemplates the use of such mixed functional diamines in preparing the functional ionene polymers of this invention. For example, by the Michael addition with acrylamide to N,N-dimethylpropylenediamine the following mixed functional diamine may be prepared:



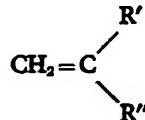
10 While a method has been described for preparing the functional ionene polymers of this invention, it is evident that other methods also clearly recommend themselves for use in preparing the polymers of this invention. For example, use may be made of a starting material from which the functional ionene polymers of this invention may be prepared directly. Such a starting material would be, for example:



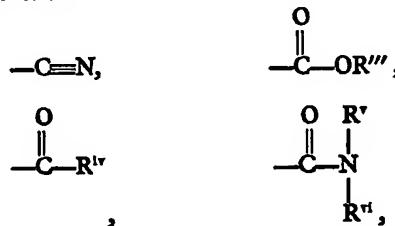
Diamines useful in preparing the functional ionene polymers of this invention may be represented by the formula:

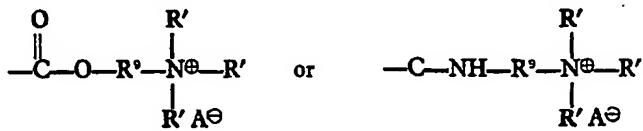


20 where at least one R' is H, although it is preferred that as many as two to all four of the R' groups be H. When R' is not H, it may be alkyl of from 1-4 carbon atoms or alkenyl of from 2-4 carbon atoms. R'' is a straight or branched alkylene group of 1-18 carbon atoms, where the carbon atom chain may be interrupted by one or more atoms of oxygen or sulfur. R'' may also be aralkylene, for example xylylene or cycloalkylene, for example cyclohexylene. Compounds capable of introducing functional groups in preparing the functional ionene polymers of this invention may be represented by the formula:



wherein R is hydrogen, halogen, alkyl, cycloalkyl, alkaryl, aralkyl, heterocyclic or substituted heterocyclic; and R" is a radical of the formula:





where R' and R° are as defined above;

R''' is alkyl, cycloalkyl or alkoxyalkyl;

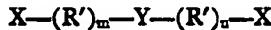
$\text{R}^{\prime \prime}$ is alkyl, cycloalkyl, alkoxyalkyl or aryl;

5 each of R' and R° is hydrogen, alkyl, cycloalkyl, aryl, alkaryl or alkoxyalkyl; and

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A^{\ominus} is an anion.

Dihalide compounds useful in preparing the functional ionene polymers of this invention may be represented by the formula:



10 where X is halogen, preferably Br or Cl; 10
 R' is a CH_2 group and/or a substituted CH_2 group in which one of the hydrogen atoms of the group is replaced by alkyl or hydroxymethyl; 10
 m and n are integers of 1 to 10 and may be the same or different; and 10
 Y is as defined above.

15 Examples of dihalide compounds that would be useful in preparing the functional ionene polymers of this invention include bis(chloromethyl)ether, bis(2-chloroethyl)- 15
 ether, bis(2-chloropropyl)ether, bis(4-chlorobutyl)ether, oxy-3-bis(2-chloropropanol-1), bis(2-chloroethyl)sulfide, bis(2-chloroethyl)sulfoxide, bis(2-chloroethyl)sulfone, bis(3-chloropropyl)sulfide, bis(2-chloropropyl)sulfone, bis(2-chloroethoxy)ethane, 20
 1,2-bis(2-chloropropoxy)propane, 1,3-dichloropropane-2, 1,3-dichloropropanol-2, 20
 bis(2-chloromethyl)amine, 1,4-bis(chloromethyl)benzene, 1,5-bis(chloromethyl)- 20
 naphthalene, 9,10 - bis(chloromethyl)anthracene, chloroethyl - chloromethyl ether, 25
 1 - (4 - chlorobutyl)chloromethyl ether, chloroethyl - chloromethyl sulfide, chloroethyl-chloromethylsulfoxide, and chloroethyl-chloromethyl sulfone. 25

25 The novel functional ionene polymers of this invention have been found to be 25
 useful in a number of different applications. The usefulness of these compositions for some particular purpose may variously depend upon the basic cationic nature of the polymer structure, or upon the chemical and physical properties of the functional group or groups employed in preparing the functional ionene polymers as previously described, 30 or upon both.

30 The functional ionene polymers of this invention are useful in four broad areas of application: (1) as processing aids; (2) as significant process modifiers; (3) as valuable additions to a given product; and (4) as products themselves.

35 As processing aids, the functional ionene polymers of this invention may be used 35
 as solids/liquid separation aids, particularly as coagulants and flocculants. They may be used as dewatering aids for sewage and mineral sludges. They are useful as flotation aids and as scale and deposit inhibitors. In the paper industry they find use as pigment retention aids, as drainage aids, and as sheet formation aids. The functional ionenes of this invention are also useful as chelating agents, demulsifiers, catalysts and biocides. 40

40 As significant process modifiers, the functional ionene polymers of this invention 40
 may be employed to modify the rheological properties of fluids. They may be used, for example, as friction reducers or turbulence suppressors, as mobility control agents in oilfield flooding for secondary recovery, and as gelling agents. The functional ionenes may be employed as dispersants for pigments, clays, sludge and other materials in both water and oil-based systems. 45

45 As valuable additional components of given products, the functional ionene polymers of this invention may be used as wet and dry strength resins in paper, and as 50
 functional coatings on paper, for example, electro-conductive, adhesive and photosensitive coatings. They may be used as components of various consumer products, for example, shampoos, antistatics, and cosmetics. They may be used as textile finishing products for soil release, antistatic and other uses. They may be used as detergents and as detergent additives to, for example, lubricating oils.

50 As products themselves, the functional ionene polymers of this invention may be 50
 permeable membranes for use, for example, in electrodialysis. They may be used in biomedical applications as for example, non-thrombogenic materials. They may be used as gels or films for cosmetic purposes. They may be coatings produced by electro-

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deposition. They may be used as ion-exchange or metal-chelating resins, and as poly-salt complexes. They may be used as modified plastics or as modified fibers.

Other specific uses for the functional ionene polymers of this invention which may be conveniently placed under one of the broad areas of application discussed above, are, as flame retardants, hair sprays, sequestering agents, grease thickening agents, dye mordants and dyeable assists in fibers and photographic film, emulsion stabilizers and emulsifiers, corrosion inhibitors, softening agents for fabrics and paper, silver halide peptizers and sensitizers for photographic film, agents for the isolation of proteins, printing inks and adhesives.

This invention will be further described by way of the following examples which illustrate both the preparation of representative functional ionene polymers of this invention, as well as the utilization of the polymers of this invention in the various indicated areas. These examples, are, however, merely illustrative and are not intended to in any way limit the scope of this invention.

EXAMPLE 1.

Preparation of N,N,N',N'-Tetrapropionamide-ethylenediamine (TPEDA).

The following materials and amounts were employed in the preparation:

		Amount (Grams)	Mol. Wt.	Moles
20	Ethylenediamine	192	60	3.2
	Acrylamide	896	71	12.6
	Water	896	—	—

The acrylamide monomer and a magnetic stirring bar were charged to a 3-liter resin kettle, which was fitted with a condenser, thermometer, and dropping funnel. The water was then added and the acrylamide monomer dissolved therein. The ethylenediamine was charged into the dropping funnel. When dissolution of the acrylamide monomer was completed, the temperature of the solution was raised to 20° C. The ethylenediamine was then added over a 45 minute period, during which addition the temperature was maintained between about 20° and about 33° C. by cooling. After addition of the ethylenediamine was complete, the cooling bath was removed, and the temperature of the reaction mixture was permitted to rise unimpeded. The temperature of the reaction mixture was observed to peak at about 38° C. after 15 minutes. The reaction mixture, which at that point was a deep-gold, slightly viscous solution, was stirred overnight without external heating or cooling. The following day, the resin kettle was solid with a white precipitate, which was filtered off, washed with acetone, and vacuum-dried in a heated desiccator overnight at 40° C. under a vacuum of 20 mm. of Hg. The total yield was 933.8 g., or 84% based on ethylenediamine. Theoretical yield of N,N,N',N'-tetrapropionamide-ethylenediamine (TPEDA) would be 1101 g. Product structure was consistent with NMP analysis. Other characterization analyses were undertaken on the reaction product. Parts-by-weight percentages for the atomic constituents of the reaction product were calculated and then determined by analysis, giving the following results:

	For C ₁₄ H ₂₈ O ₄ N ₆	C	H	N
45	Calculated	48.70	8.14	24.4
	Found	48.47	8.29	23.4

A test for secondary amine using NiCl₂/Cl₂/CS₂ gave negative results. Titration indicated two inflection points due to two amine functions. The moisture content was found to be less than 1% by weight. The reaction product was found to be soluble in water with heating, and insoluble in methanol, DMF, acetone and ethanol.

EXAMPLE 2.

Preparation of N,N,N',N'-tetra[3-acrylamido-3-methylbutyl trimethyl ammonium chloride]ethylenediamine (TAMBTACEDA).

The following materials and amounts were employed in the preparation:

		Amount (Grams)	Mol. Wt.	Moles
55	Ethylenediamine	6	60	0.1
	AMBTAC*	94	235	0.4
	Water	94	—	—

*AMBTAC is 3-acrylamido-3-methylbutyl trimethyl ammonium chloride.

5 The AMBTAC monomer, water and a magnetic stirring bar were charged into a 500-ml. flask fitted with thermometer, condenser and dropping funnel. The ethylenediamine was charged into the dropping funnel. After the AMBTAC monomer was dissolved, the ethylenediamine was added dropwise over a 2-minute period. During this time the temperature rose from 25° to 29° C. After the addition of ethylenediamine was complete, the reaction mixture was heated to 40° C. and held at that temperature for two hours. No precipitate formed and the reaction mixture was brought to a 75% concentration by removing a portion of the water with benzene. Acetone was then added to the reaction mixture and hygroscopic white precipitate was formed. The precipitate was dried under vacuum, which resulted in a glassy material, and this material was utilized without further treatment.

10 Product characterization using NMR analysis was consistent with the proposed structure.

EXAMPLE 3.

15 Preparation of N,N'-dimethyl-N,N'-dipropionamido-ethylenediamine (DMDPEDA).

The following materials and amounts were used in the preparation:

		Amount (Grams)	Mol. Wt.	Moles	
20	N,N'-dimethylethylenediamine (DMEDA)	88	88	1.0	20
	Acrylamide	142	71	2.0	
	Water	142	—	—	

25 The acrylamide monomer and a magnetic stirring bar were charged into a 500-ml. 3-neck flask fitted with thermometer, condenser and dropping funnel. The water was then added and stirring initiated to solubilize the acrylamide monomer. The N,N'-dimethylethylenediamine (DMEDA) was then charged into the dropping funnel. After the acrylamide monomer was dissolved, the DMEDA was added over a 45-minute period, with the temperature being maintained within the range 30° to 35° C. with cooling. After the addition was completed, the cooling bath was removed and the temperature allowed to rise to 36° C. The reaction mixture was stirred overnight with external heating or cooling. The following day, the reaction flask was found to be solid with a white precipitate, which was filtered off and washed with acetone. The white precipitate was vacuum-dried in a heated desiccator overnight to yield 134.5 grams, which represents a 59.5% yield based on DMEDA.

30 Product characterization using NMR analysis was consistent with the proposed structure.

35 Other characterization analyses were undertaken on the reaction product. Parts-by-weight percentages for the atomic constituents of the reaction product were calculated and determined by analysis, giving the following results:

40	For C ₁₀ H ₂₂ O ₂ N ₄	C	H	N	
	Calculated	52.2	9.57	24.3	40
	Found	50.4	9.89	24.1	

The melting point for the reaction product was determined to be 120° C.

EXAMPLE 4.

45 Functional ionene reaction product of N,N,N',N'-tetrapropionamido-ethylenediamine (TPEDA) and 1,4-dibromobutane (DBB).

The following materials and amounts were used in the preparation:

		Amount (Grams)	Mol. Wt.	Moles	
50	TPEDA	17.2	344	0.05	50
	DBB	10.8	216	0.05	
	Water	28.0	—	—	

55 The TPEDA and a magnetic stirring bar were charged into a 100 ml. 3-neck flask fitted with thermometer, condenser and dropping funnel. Once the TPEDA was dissolved the DBB was added, and the reaction mixture was then heated to reflux (95—100° C.) and held at that temperature for 136 hours. For the purpose of analytical procedures, a white solid was recovered from the aqueous solution by pouring the solution into acetone.

Product characterization by means of NMR analysis confirmed the expected structure. Other characterization analyses were performed. Parts-by-weight percentages for the atomic constituents of the reaction product were calculated and determined by analysis giving the following results:

5	For $C_{12}H_{36}O_4H_6Br_2$	C	H	N	5
	Calculated	38.6	6.44	15.0	
	Found	41.3	6.67	14.6	

The moisture content of the reaction product was determined to be 8.2% by weight.

EXAMPLE 5.

Functional ionene reaction product of N,N'-dimethyl-N,N'-dipropionamide-ethylene-diamine (DMDPEDA) and 1,4-dibromobutane (DBB). The following materials and amounts were used in the preparation:

	Amount (Grams)	Mol. Wt.	Moles
DMDPEDA	100	230	0.435
DBB	94	216	0.435
Water	194	—	—

The DMDPEDA, DBB and water were charged into a 500 ml. flask fitted with a thermometer and condenser. Stirring was accomplished with a magnetic stirring bar. The solution of the ingredients was heated to reflux (95–100° C.) and maintained for five days. Subsequent to heating, the solution was concentrated and poured into methanol, from which a white precipitate was recovered.

Product characterization using NMR analysis gave the expected structure. Additional characterization analyses were undertaken on the functional ionene reaction product. Parts-by-weight percentages for the atomic constituents of the reaction product were calculated and determined by analysis, giving the following results:

30	For $C_{14}H_{30}N_4O_2Br_2$	C	H	N	
	Calculated	37.7	6.72	12.6	
	Found	41.6	6.86	11.5	30

Moisture content of the reaction product was observed to be 9.0% by weight. Onset of decomposition for the reaction product was observed to be 117° C.

EXAMPLE 6.

Functional ionene reaction product of N,N,N',N' -tetra-(3-acrylamido-3-methylbutyl trimethyl ammonium chloride) ethylenediamine (TAMBTACEDA) and 1,4-dibromo-butane (DBB).

The following materials and amounts were used in the preparation:

		Amount (Grams)	Mol Wt	Moles	
40	TAMBTACEDA	25	1000	0.025	40
	DBB	5.4	216	0.025	
	Water	22.1	—	—	

The TAMB TACEDA, DBB and water were combined in a 100-ml. 1-neck flask. The reaction mixture was heated at reflux (95–100° C.) for five days. After the heating was complete, the solution was concentrated on a rotary evaporator and a solid was precipitated by the addition of acetone. NMR analysis confirmed the expected structure. Additional characterization analyses on the reaction product was undertaken. Parts-by-weight percentages for the atomic constituents of the reaction product were calculated and determined by analysis, giving the following results:

50	For $C_{50}H_{108}N_{10}O_4Cl_4Br_2$	C	H	N	50
	Calculated	49.4	8.91	11.5	
	Found	42.6	9.01	10.5	

The moisture content of the reaction product was determined to be 14.6% by weight.

EXAMPLE 7.
Electroconductivity.

In this method the electroconductivity of the functional ionene polymers was tested as resistance to the flow of an electrical current by the polymers when coated on a flat substrate. In this example paper was used as such a substrate.

An aqueous solution of the polymer to be tested was prepared and formed onto a paper substrate suitable for applying electroconductive coatings (such as Bergstrom's copy paper base stock 20 lb./ream: 3000 ft.²) by means of a Meyer wire-wound draw rod. The variations in the coating thicknesses were obtained with changes in the size of the draw rod used. The coated paper was dried to the touch in an oven maintained at 105° C. After drying, the paper was conditioned in a constant-conditions room for at least 16 hours, after which the conditioned paper was placed in a chamber maintained at a relative humidity of 13%, where the paper was conditioned for at least 24 hours. The coated paper (3.175 inches wide cut and measured) was then passed through a Keithly Resistivity Adaptor, with the coated side down, where a voltage of 100 volts was applied. The electrical current passing through the surface of the coated paper substrate was read using a Keithly Electrometer. The electrical current was read in amperes, and the surface resistivity was calculated from the following equation:

$$\text{Surface resistivity (ohms)} = 53.4 \times V/A$$

V = Applied voltage

A = Electrometer reading—in amperes

The results of the test for electroconductivity are summarized in the table below:

25	Polymer	Coat Weight lbs./3000 ft. ²	Surface Resistivity At		25
			13% R.H.	>10 ¹⁵	
30	TPEDA/DBB ¹	1.6	>10 ¹⁵	>10 ¹⁵	30
	"	0.95	>10 ¹⁵	>10 ¹⁵	
	"	0.79	>10 ¹⁵	>10 ¹⁵	
	"	0.48	>10 ¹⁵	>10 ¹⁵	
	"	0.16	>10 ¹⁵	>10 ¹⁵	
35	DMDPEDA/DBB ²	1.6	4.45 × 10 ¹⁵	5.34 × 10 ¹⁵	35
	"	1.3	5.34 × 10 ¹⁵	>10 ¹⁵	
	"	0.95	>10 ¹⁵	>10 ¹⁵	
	"	0.64	>10 ¹⁵	>10 ¹⁵	
	"	0.16	>10 ¹⁵	>10 ¹⁵	
40	TAMBTACEDA/DBB ³	1.4	8.34 × 10 ¹⁵	1.07 × 10 ¹⁵	40
	"	1.1	1.07 × 10 ¹⁵	1.41 × 10 ¹⁵	
	"	0.95	1.41 × 10 ¹⁵	1.98 × 10 ¹⁵	
	"	0.64	1.98 × 10 ¹⁵	3.56 × 10 ¹⁵	
	"	0.48	3.56 × 10 ¹⁵	>10 ¹⁵	

¹ TPEDA/DBB = The functional ionene reaction product of Example 4.

² DMDPEDA/DBB = The functional ionene reaction product of Example 5.

³ TAMBTACEDA/DBB = The functional ionene reaction product of Example 6.

EXAMPLE 8.
Dry Strength.

The functional ionene polymers were evaluated for dry strength enhancing properties by preparing a series of hand sheets on a Noble Wood hand sheet forming machine, using the various polymer additives. The hand sheets were conditioned at 50% relative humidity at 70° F. for a minimum of 24 hours. The hand sheets were then tested for burst and tensile strength, with the values for these reported as a percentage increase over the blank. The blank hand sheets were prepared under the same conditions, except that no polymer dry strength additives were used.

The pulp stock used in preparing the hand sheets was bleached, hardwood sulfite pulp. The freeness was 650 ml. Schopper Reigler. Two percent alum was added. The dry strength polymers were added to the headbox and mixed there for 3 minutes. The preparation was done in acid and alkaline media, with the headbox and sheet mold pH's being adjusted to 4.5 and 8.6 with 0.5 NH₄SO₄. There was no white water circulation during the preparation. The sheets were dried for 5 minutes at 230° F. before conditioning and evaluating. The burst strength was tested by a Mullen Tester ('Mullen' is a trade mark) according to TAPPI standard test procedure T403. The tensile strength was tested by a TMI instrument in accordance with TAPPI standard test procedure T404.

The results for the dry strength testing procedure are summarized in the following table.

		pH=4.5						
		Feedrate lbs./ton	Dry Tensile	% Over Blank	Burst	% Over Blank		
5	<u>Polymer</u>							
	TPEDA/DBB	—	6.7	—	9.2	—		
	DMDPEDA/DBB	20	6.9	3	10.2	10		
10	TAMBTACEDA/DBB	20	7.1	6	12.0	30		
	TPEDA/DBB	20	6.7	—	11.0	20		
	DMDPEDA/DBB	—	6.3	—	12.0	—		
15	TAMBTACEDA/DBB	20	6.5	3	11.7	—2.5		
	DMDPEDA/DBB	20	6.8	8	12.5	4		
	TAMBTACEDA/DBB	20	6.9	10	13.5	12.5		

EXAMPLE 9.

Wet Strength.

The wet-strength-enhancing properties of the ionene polymers were evaluated in a manner similar to that described in Example 9. A 50/50 bleached, soft wood and hard wood Kraft pulp was beaten to a Schopper Reigler freeness of 750 ml. Portions of the pulp were mixed with the wet-strength additive polymers at the percentage feed rate shown in the table below (based on pulp solids). The mixing was accomplished by means of a Heller stirrer for one minute, then transferred to the proportioner of a Noble Wood hand sheet forming machine. The pulp was formed into hand sheets of about 30 lbs. per 3,000 ft.² basis weight, dried 5 minutes at 232° F., then cured at 105° C. for 2 hours. A blank hand sheet was prepared in the same manner, except that no wet-strength additive was used. The hand sheets were conditioned at 72° F. and 50% relative humidity for at least 24 hours. The sheets were tested on a TMI instrument for dry tensile strength as well as wet tensile strength after a 10 minute soaking in distilled water. The ratio of wet tensile strength to dry tensile strength expressed as a percentage equals percent wet strength.

The results for the testing procedure just described are summarized in the table below.

		% Wet Strength, pH=4.5						
		0.5% Feedrate	1.0% Feedrate	2.0% Feedrate				
35	<u>Polymer</u>							
	Blank	7.3	—	—				
	TPEDA/DBB	7.4	7.4	6.2				
40	"	7.1	8.0	8.4				
	"	6.3	6.2	5.8				
	"	8.0	8.4	8.8				
45	"	8.1	8.0	9.4				
	DMDPEDA/DBB	7.4	6.0	7.4				
	"	7.1	8.9	9.1				
50	"	7.2	8.8	10.7				
	"	7.6	9.0	9.7				
	TAMBTACEDA/DBB	6.3	6.6	7.6				
% Wet Strength, pH=7.5								
55	<u>Polymer</u>							
	Blank	8.6	—	—				
	TPEDA/DBB	7.5	7.8	10.5				
55	"	6.6	7.6	8.0				
	"	8.0	8.5	8.0				
	"	7.1	7.4	7.9				
55	DMDPEDA/DBB	8.0	8.2	8.4				
	"	7.0	7.1	7.4				
	"	8.2	6.5	7.0				
55	"	7.6	6.5	8.5				
	"	8.5	7.5	8.1				
	TAMBTACEDA/DBB	7.7	6.5	7.8				

EXAMPLE 10.
Corrosion Inhibition.

Corrosion inhibition properties for the functional ionene polymers were determined by means of potentiostatic polarization. This method provides a simple and direct means of quantifying metallic corrosion by measuring the polarizing effect of an applied current on the natural equilibrium of the partial anodic and cathodic currents inherent in the oxidation/reduction reaction of corrosion, and the resulting displacement of the potential of a metal electrode which is undergoing such corrosion. The applied current is measured as a function of the potential of the corroding electrode, which is controlled by means of a potentiostat. In particular, the Tafel slope extrapolation procedure was employed to determine corrosion rates. The potential of the working (corroding) electrode was plotted against the logarithm of the applied current. The resulting curve was linear in the so-called Tafel region and this was extrapolated to the corrosion potential value, which is the potential at which the metal of the working electrode corrodes in an aerated aqueous environment. The intercept point corresponds to the corrosion rate of the system expressed in terms of current density. In order to convert this value to the more conventional expression of corrosion rate in terms of mils per year (mpy) or milligrams per square decimeter per day (mdd), the following conversion was used:

$$\begin{aligned} \text{mpy} &= 0.46 I \mu\text{a}/\text{cm}^2 \\ \text{mdd} &= 2.5 I \mu\text{a}/\text{cm}^2 \end{aligned}$$

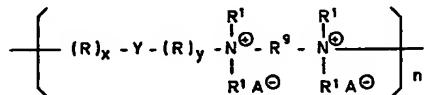
where $I \mu\text{a}/\text{cm}^2$ is the current density at the point of intercept expressed as milliamperes per square centimeter. This conversion is based on the relationship of the current density at the equilibrium or corrosion potential, and the amount of iron consumed by corrosion [expressed as milligram per square decimeter of surface per day (mdd) or as mils per year (mpy)] which may be derived through Faraday's Law. For example, a current density of 4.0×10^{-7} amperes/cm² is equal to 1.0 mg/dm²/day.

The tests were conducted in synthetic Pittsburgh water at an initial pH of 7.0, with a final pH as indicated in the table below. Steel electrodes were used in the polarization test cells and the corrosion inhibitor concentrations were calculated on the basis of active material. The results of the potentiostatic polarization tests are illustrated in the table of data below.

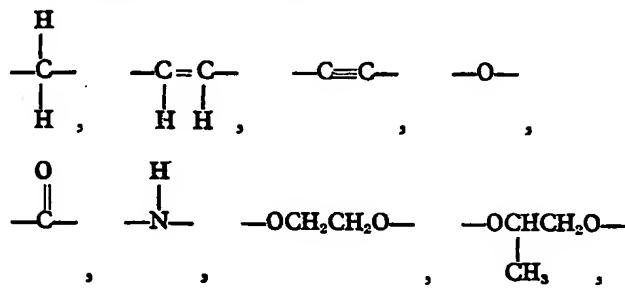
			Dosage ppm	Final pH	Corrosion Rate mdd	
35	<u>Polymer</u>	TPEDA	100	7.7	61	35
		"	500	7.6	69	
40	TPEDA/DBB	100	7.6	59	40	
		500	7.3	65		
45	DMDPEDA	100	7.8	59	45	
		500	7.6	110		
50	TAMB/TACEDA	100	7.7	71	50	
		500	7.8	71		
55	DMDPEDA/DBB	100	7.6	81	55	
		500	7.3	90		
60	TAMB/TACEDA/DBB	100	7.6	50	60	
		500	7.5	66		
65	Control "	—	—	90—95	65	
		—	—	90—95		

WHAT WE CLAIM IS:—

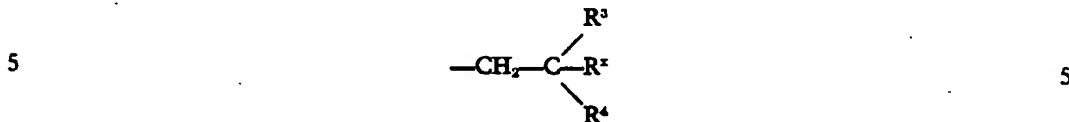
1. A polymer represented by the formula:



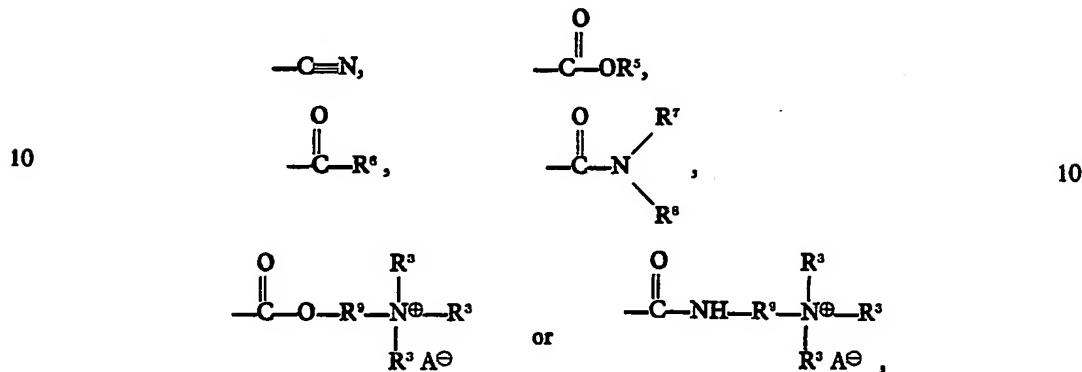
in which R^1 is an alkylene group;
 R represents the group CH_2 and/or a substituted CH_2 group in which one of the hydrogen atoms of the group is replaced by alkyl or hydroxymethyl;
 Y is



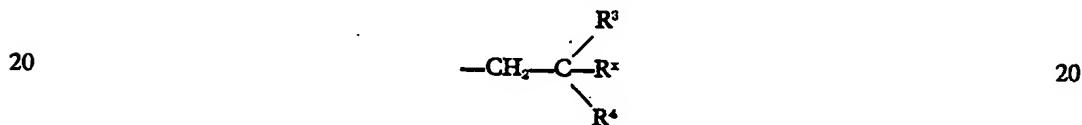
—OCH₂O, —S—, —SO—, —SO₂— or arylene; in which R¹ is a C₁₋₄ alkyl or C₂₋₄ alkenyl radical or a radical of formula:



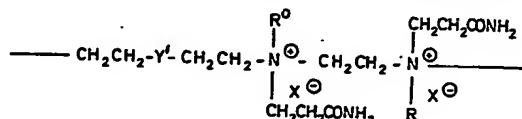
R^2 is hydrogen or C_{1-4} alkyl,
 R^3 is hydrogen, halogen, alkyl, cycloalkyl, aryl, alkaryl, or aralkyl, and
 R^4 is



where R^3 and R^6 are as defined above;
 R^5 is alkyl, cycloalkyl, or alkoxyalkyl;
 R^6 is alkyl, cycloalkyl, alkoxyalkyl or aryl;
each of R^7 and R^8 is, independently of the other, hydrogen, alkyl, cycloalkyl, aryl, alkaryl, aralkyl, or alkoxyalkyl;
 A^\ominus is an anion;
 x and y are integers from 1 to 10; and
 n is an integer; provided that at least one R^1 is a group of formula:

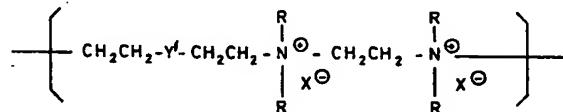


2. A polymer having recurring units represented by the formula:

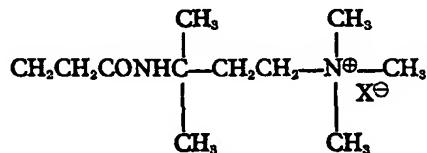


in which R^0 is CH_3 or $CH_2CH_2CONH_2$; X is Cl or Br; and Y' is oxygen or nothing.

3. A polymer having recurring units represented by the formula:



in which R is



5 X is Cl or Br; and Y' is oxygen or nothing.

4. A polymer as claimed in claim 1, when prepared by a process substantially as hereinbefore described in any one of Examples 1 to 6.

10 5. A method of enhancing the dry strength properties of paper comprising the step of adding to the pulp stock used in preparing the said paper, an effective amount of a polymer composition as claimed in any one of claims 1 to 4.

6. A method of enhancing the wet strength properties of paper comprising the step of adding to the pulp stock used in preparing the said paper, an effective amount of a polymer composition as claimed in any one of claims 1 to 4.

15 7. A method of inhibiting the corrosion of metal-bearing surfaces in contact with an aqueous solution comprising adding to the said solution an effective amount of a polymer composition as claimed in any one of claims 1 to 4.

8. A coated paper product comprising a paper substrate having applied thereto an electroconductive coating comprising a polymer composition as claimed in any one of claims 1 to 4.

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